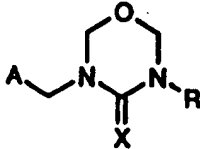




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : A01N 43/88, 51/00 // (A01N 43/88, 53:00, 43:707, 43:653, 43:54, 43:36, 37:22) (A01N 51/00, 53:00, 43:707, 43:653, 43:54, 43:36, 37:22)</p>	A1	<p>(11) International Publication Number: WO 97/22254</p> <p>(43) International Publication Date: 26 June 1997 (26.06.97)</p>
<p>(21) International Application Number: PCT/EP96/05489</p> <p>(22) International Filing Date: 7 December 1996 (07.12.96)</p> <p>(30) Priority Data: 3570/95 18 December 1995 (18.12.95) CH 2502/96 14 October 1996 (14.10.96) CH</p> <p>(71) Applicant (for all designated States except US): NOVARTIS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basle (CH).</p> <p>(72) Inventor; and (75) Inventor/Applicant (for US only): ELMSHEUSER, Hans [DE/DE]; Ringstrasse 24, D-79595 Rümmingen (DE).</p> <p>(74) Common Representative: NOVARTIS AG; Patent and Trade-mark Dept., Klybeckstrasse 141, CH-4002 Basle (CH).</p>		<p>(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>
<p>(54) Title: PESTICIDAL COMPOSITION</p> <p>(57) Abstract</p> <p>A composition for controlling simultaneously insects or representatives of the order Acarina and microorganisms, which composition comprises at least one compound of formula (I), wherein A is an unsubstituted or mono- to tetra-substituted aromatic or non-aromatic, monocyclic or bicyclic, heterocyclic radical, one or two of the substituents of A being selected from the group consisting of: halo-C₁-C₃alkyl, cyclopropyl, halocyclopropyl, C₂-C₃alkenyl, C₂-C₃alkynyl, halo-C₂-C₃alkenyl, halo-C₂-C₃alkynyl, halo-C₁-C₃alkoxy, C₁-C₃alkylthio, halo-C₁-C₃alkylthio, allyloxy, propargyloxy, allylthio, propargylthio, haloallyloxy, haloallylthio, cyano and nitro, and from one to four of the substituents of A being selected from the group consisting of: C₁-C₃alkyl, C₁-C₃alkoxy and halogen; R is hydrogen, C₁-C₆alkyl, phenyl-C₁-C₄alkyl, C₃-C₆cycloalkyl, C₂-C₆alkenyl or C₂-C₆alkynyl; and X is N-NO₂ or N-CN, or, where appropriate, a tautomer thereof, in each case in free form or in salt form, at least one microbicidal compound, and at least one adjuvant, and, where appropriate, at least one further insecticidal compound, a method of controlling pests and microorganisms, a process for the preparation of the composition, its use and plant propagation material treated therewith are described.</p> <div style="text-align: right;">  <p>(I)</p> </div>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

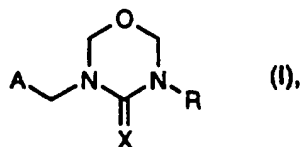
AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SR	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

Pesticidal Composition

The present invention relates to a composition that comprises one or more insecticidal or acaricidal compounds and one or more fungicidal compounds and that is suitable for controlling simultaneously insects and/or representatives of the order Acarina and microorganisms, especially phytopathogenic fungi, for example on plants, to a method of controlling those pests, to a process for the preparation of the appropriate composition and to the use thereof.

Certain mixtures of active ingredients for controlling pests are described in the literature. The biological properties of those known mixtures are not entirely satisfactory in the area of pest control and there is therefore a need to make available other mixtures, especially those having synergistic properties, for example synergistic pesticidal properties, especially for controlling insects and representatives of the order Acarina and microorganisms. That problem is solved according to the invention by the provision of the present composition.

The invention accordingly relates to a composition for controlling insects or representatives of the order Acarina and microorganisms, which composition comprises at least one compound of formula



wherein

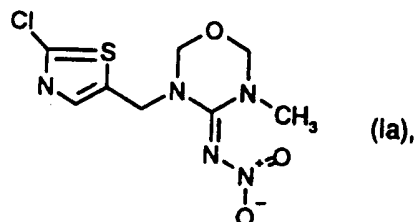
- A** is an unsubstituted or mono- to tetra-substituted aromatic or non-aromatic, monocyclic or bicyclic, heterocyclic radical, one or two of the substituents of A being selected from the group consisting of: halo-C₁-C₃alkyl, cyclopropyl, halocyclopropyl, C₂-C₃alkenyl, C₂-C₃alkynyl, halo-C₂-C₃alkenyl, halo-C₂-C₃alkynyl, halo-C₁-C₃alkoxy, C₁-C₃alkylthio, halo-C₁-C₃alkylthio, allyloxy, propargyloxy, allylthio, propargylthio, haloallyloxy, haloallylthio, cyano and nitro, and from one to four of the substituents of A being selected from the group consisting of: C₁-C₃alkyl, C₁-C₃alkoxy and halogen;
- R** is hydrogen, C₁-C₆alkyl, phenyl-C₁-C₄alkyl, C₃-C₆cycloalkyl, C₂-C₆alkenyl or C₂-C₆alkynyl; and

X is N-NO₂ or N-CN,

or, where appropriate, a tautomer thereof, in each case in free form or in salt form,

at least one microbicidal compound, and at least one adjuvant, and, where appropriate, at least one further insecticidal compound.

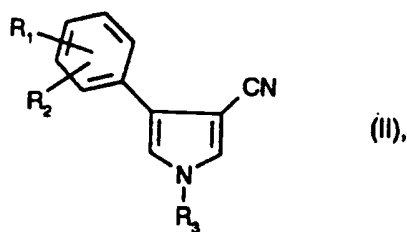
Preference is given especially to a composition that comprises the compound of formula



and one or more compounds selected from the substance classes consisting of azoles, cyanopyrroles and acylalanines.

Preference is given likewise to compositions that comprise in addition to at least one compound of formula (I) at least one further compound selected from the active ingredient class of the pyrethroids, and to compositions that comprise one or more compounds selected from hymexazole, triazoxide, acylalanines, anilinopyrimidines, azoles and cyanopyrroles.

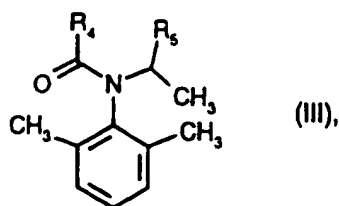
There are understood by cyanopyrroles, for example, compounds of formula



wherein R₁ and R₂ are each independently of the other hydrogen, fluorine, chlorine, bromine or trifluoromethyl, or two radicals R₁ and R₂ in the ortho-position relative to one another are -O-CF₂-O-, and R₃ is hydrogen or a group -C(=O)-C₁-C₄alkyl;

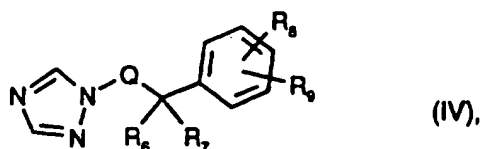
by acylalanines, for example, compounds of formula

- 3 -



wherein R_4 and R_5 are organic radicals; R_4 is preferably C_1 - C_4 alkoxy- C_1 - C_4 alkyl, phenyl, benzyl or furyl and R_5 is preferably $-C(=O)-C_1$ - C_4 alkyl;

by azoles, for example, compounds of formula



wherein R_6 and R_7 are each independently of the other hydrogen, hydroxy, cyano, C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_2 - C_4 alkenyloxy, C_1 - C_4 alkoxy- C_1 - C_4 alkyl, halo- C_1 - C_4 alkoxy- C_1 - C_4 alkyl, 4-chlorophenyl-substituted C_1 - C_4 alkyl, cyclopropyl- C_1 - C_4 alkyl, phenyl that is unsubstituted or mono- or di-substituted by halogen, or R_6 and R_7 , together with the carbon atom to which they are bonded, form a three- to six-membered ring containing one or two hetero atoms, preferably nitrogen or oxygen, especially a 5-membered ring containing two oxygen atoms, that is unsubstituted or mono- or poly-substituted by halogen, C_1 - C_4 alkyl, halo- C_1 - C_4 alkyl, C_1 - C_4 alkoxy or by halo- C_1 - C_4 alkyl,

R_8 and R_9 are each independently of the other hydrogen, fluorine, chlorine, bromine, cyano, nitro or 4-chlorophenoxy,

Q is $[C(R_{10})_2]_n$,

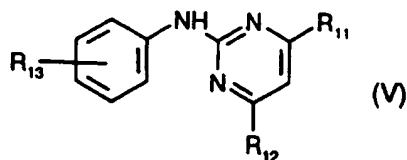
the two radicals R_{10} are each independently of the other hydrogen, phenoxy or 4-chlorophenoxy and

n is 1 or 2,

and bitertanol, diniconazole, epoxiconazole (BAS 480F), fluquiconazole, flusilazole, imazalil, imibenconazole, ipconazole, metconazole, pefurazoate, prochloraz, SSF-109, tebuconazole, triticonazole, triadimefon, triadimenol, triflumizole and uniconazole; and,

by anilinopyrimidines, compounds of formula

- 4 -



wherein R₁₁ and R₁₂ are each independently of the other hydroxy, halogen, cyano, C₁-C₈-alkyl, C₃-C₆-cycloalkyl, C₃-C₆-cycloalkenyl, C₂-C₈-alkenyl, C₂-C₈-alkynyl, phenyl-substituted C₁-C₄-alkyl, cyclopropyl-C₁-C₄-alkyl, C₁-C₄-alkoxy or C₂-C₄-alkenyloxy; and

R₁₃ is hydrogen, cyano, halogen, C₁-C₈-alkyl, halo-C₁-C₈-alkyl, C₁-C₈-alkoxy, halo-C₁-C₈-alkoxy, C₃-C₆-cycloalkyl or C₂-C₈-alkenyl.

Pyrethroids are to be understood to be, preferably, those listed in The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London. There may be mentioned by way of example: Tefluthrin, mentioned on page 953 of the said Pesticide Manual, Cypermethrin, mentioned on page 259, beta-Cyfluthrin, mentioned on page 250, Deltamethrin, mentioned on page 287 and tau-Fluvalinate, mentioned on page 515. Tefluthrin is preferred.

Some of the compounds of formula (I) may be in the form of tautomers. When, for example, R is hydrogen, corresponding compounds of formula (I), i.e. those having a 3-H-4-imino-perhydro-1,3,5-oxadiazine partial structure, are in equilibrium with the respective tautomers having a 4-amino-1,2,5,6-tetrahydro-1,3,5-oxadiazine partial structure. Accordingly, hereinbefore and hereinafter, where appropriate the compounds of formula (I) are to be understood to include corresponding tautomers, even if the latter are not specifically mentioned in each case.

Compounds of formula (I) having at least one basic centre are capable, for example, of forming acid addition salts. Those salts are formed, for example, with strong inorganic acids, such as mineral acids, for example perchloric acid, sulfuric acid, nitric acid, nitrous acid, a phosphoric acid or a hydrohalic acid, with strong organic carboxylic acids, such as unsubstituted or substituted, for example halo-substituted, C₁-C₄-alkanecarboxylic acids, for example acetic acid, saturated or unsaturated dicarboxylic acids, for example oxalic, malonic, succinic, maleic, fumaric or phthalic acid, hydroxycarboxylic acids, for example ascorbic, lactic, malic, tartaric or citric acid, or benzoic acid, or with organic sulfonic acids, such as unsubstituted or substituted, for example halo-substituted, C₁-C₄-alkane- or aryl-sulfonic acids, for example methane- or p-toluene-sulfonic acid. Furthermore, compounds of

formula (I) having at least one acid group are capable of forming salts with bases. Suitable salts with bases are, for example, metal salts, such as alkali metal or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower alkyl-amine, for example ethyl-, diethyl-, triethyl- or dimethyl-propyl-amine, or a mono-, di- or tri-hydroxy-lower alkylamine, for example mono-, di- or tri-ethanolamine. In addition, corresponding internal salts may also be formed. Preference is given within the scope of the invention to agrochemically advantageous salts. In view of the close relationship between the compounds of formula (I) in free form and in the form of their salts, any reference hereinbefore or hereinafter to the free compounds of formula (I) or to their salts is to be understood as including also the corresponding salts or the free compounds of formula (I), where appropriate and expedient. The same applies in the case of tautomers of compounds of formula (I) and the salts thereof. The free form is generally preferred in each case.

Unless otherwise defined, the general terms used hereinbefore and hereinafter have the following meanings:

Suitable as heteroatoms in the basic ring structure of the heterocyclic radical A of compounds of formula (I) are any elements of the Periodic Table that are capable of forming at least two covalent bonds.

Halogen - as a group *per se* and as a structural element of other groups and compounds, such as haloalkyl, haloalkylthio, haloalkoxy, halocyclopropyl, haloalkenyl, haloalkynyl, haloallyloxy and haloallylthio, - is fluorine, chlorine, bromine or iodine, especially fluorine, chlorine or bromine, more especially fluorine or chlorine, especially chlorine.

Unless otherwise defined, carbon-containing groups and compounds each contain from 1 up to and including 6, preferably from 1 up to and including 3, especially 1 or 2, carbon atoms.

Cycloalkyl is cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, especially cyclopropyl. Cycloalkenyl is cyclopropenyl, cyclobutenyl, cyclopentenyl or cyclohexenyl, especially cyclopropenyl.

Alkyl - as a group *per se* and as a structural element of other groups and compounds, such as phenylalkyl, haloalkyl, alkoxy, haloalkoxy, alkylthio and haloalkylthio, - is, in each case taking due account of the number of carbon atoms contained in the group or compound in

- 6 -

question, either straight-chained, i.e. methyl, ethyl, propyl, butyl, pentyl or hexyl, or branched, e.g. isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, neopentyl or isohexyl.

Alkenyl, haloalkenyl, alkenyloxy, alkynyl and haloalkynyl are straight-chained or branched and each contain two or, preferably, one unsaturated carbon-carbon bond(s). The double or triple bonds of those substituents are separated from the remainder of the compound I preferably by at least one saturated carbon atom. There may be mentioned by way of example allyl, methallyl, but-2-enyl, but-3-enyl, propargyl, but-2-ynyl and but-3-ynyl.

Halo-substituted carbon-containing groups and compounds, such as haloalkyl, haloalkylthio, haloalkoxy, halocyclopropyl, haloalkenyl, haloalkynyl, haloallyloxy and haloallylthio, may be partially halogenated or perhalogenated, the halogen substituents in the case of multiple halogenation being identical or different. Examples of haloalkyl - as a group *per se* and as a structural element of other groups and compounds, such as haloalkylthio and haloalkoxy, - are methyl mono- to tri-substituted by fluorine, chlorine and/or by bromine, such as CHF_2 or CF_3 ; ethyl mono- to penta-substituted by fluorine, chlorine and/or by bromine, such as CH_2CF_3 , CF_2CF_3 , CF_2CCl_3 , CF_2CHCl_2 , CF_2CHF_2 , CF_2CFCl_2 , CF_2CHBr_2 , CF_2CHClF , CF_2CHBrF or CClFCHClF ; propyl or isopropyl mono- to hepta-substituted by fluorine, chlorine and/or by bromine, such as $\text{CH}_2\text{CHBrCH}_2\text{Br}$, $\text{CF}_2\text{CHF}_2\text{CF}_3$, $\text{CH}_2\text{CF}_2\text{CF}_3$, $\text{CF}_2\text{CF}_2\text{CF}_3$ or $\text{CH}(\text{CF}_3)_2$; and butyl, or one of the isomers of butyl, mono- to nona-substituted by fluorine, chlorine and/or by bromine, such as $\text{CF}(\text{CF}_3)\text{CH}_2\text{CF}_3$, $\text{CF}_2(\text{CF}_2)_2\text{CF}_3$ or $\text{CH}_2(\text{CF}_2)_2\text{CF}_3$. Examples of haloalkenyl are 2,2-difluoroethen-1-yl, 2,2-dichloroethen-1-yl, 2-chloroprop-1-en-3-yl, 2,3-dichloroprop-1-en-3-yl and 2,3-dibromoprop-1-en-3-yl. Examples of haloalkynyl are 2-chloroprop-1-yn-3-yl, 2,3-dichloroprop-1-yn-3-yl and 2,3-dibromoprop-1-yn-3-yl. Examples of halocyclopropyl are 2-chlorocyclopropyl, 2,2-difluorocyclopropyl and 2-chloro-2-fluoro-cyclopropyl. Examples of haloallyloxy are 2-chloroprop-1-en-3-yloxy, 2,3-dichloroprop-1-en-3-yloxy and 2,3-dibromoprop-1-en-3-yloxy. Examples of haloallylthio are 2-chloroprop-1-en-3-ylthio, 2,3-dichloroprop-1-en-3-ylthio and 2,3-dibromoprop-1-en-3-ylthio.

In phenylalkyl, an alkyl group bonded to the remainder of the compound in question is substituted by a phenyl group, the alkyl group preferably being straight-chained and the phenyl group preferably being bonded in a position higher than the α -position, especially in the ω -position, of the alkyl group; examples are benzyl, 2-phenylethyl and 4-phenylbutyl.

Preferred forms within the scope of the invention are compositions that comprise a compound of formula (I) wherein:

(1) A is an unsubstituted or mono- to tetra-substituted, aromatic or non-aromatic, monocyclic or bicyclic, heterocyclic radical, one or two of the substituents of A being selected from the group consisting of: halo-C₁-C₃alkyl, cyclopropyl, halocyclopropyl, C₂-C₃alkenyl, C₂-C₃alkynyl, halo-C₂-C₃alkenyl, halo-C₂-C₃alkynyl, halo-C₁-C₃alkoxy, C₁-C₃alkylthio, halo-C₁-C₃alkylthio, allyloxy, propargyloxy, allylthio, propargylthio, haloallyloxy, haloallylthio, cyano and nitro, and from one to four of the substituents of A being selected from the group consisting of: C₁-C₃alkyl, C₁-C₃alkoxy and halogen;

R is hydrogen, C₁-C₆alkyl, C₃-C₆cycloalkyl, C₂-C₆alkenyl or C₂-C₆alkynyl; and

X is N-NO₂ or N-CN;

(2) the basic ring structure of A consists of a ring having 5 or 6 ring members to which a further ring having 5 or 6 ring members may be fused,

especially a ring having 5 or, preferably, 6 ring members;

(3) the basic ring structure of A is unsaturated,

more especially contains one double bond or, preferably, from 2 to 4 double bonds, which are preferably conjugated,

preferably 2 double bonds, which are preferably conjugated,

and is especially aromatic;

(4) the basic ring structure of A contains from 1 up to and including 4, especially from 1 up to and including 3, more especially 1 or 2, hetero atoms, preferably 1 hetero atom;

(5) the basic ring structure of A contains 1, 2 or 3 hetero atoms selected from the group consisting of oxygen, sulfur and nitrogen, not more than one of the hetero atoms present in the basic ring structure being an oxygen atom and not more than one of the hetero atoms present in the basic ring structure being a sulfur atom,

especially 1, 2 or 3 hetero atoms selected from the group consisting of oxygen, sulfur and nitrogen, not more than one of the hetero atoms present in the basic ring structure being an oxygen or a sulfur atom,

preferably at least one nitrogen atom;

(6) A is bonded to the remainder of the compound I via a carbon atom of its basic ring structure;

(7) A is unsubstituted or mono- or di-substituted by substituents selected from the group consisting of halogen, C₁-C₃alkyl, halo-C₁-C₃alkyl, C₁-C₃alkoxy and halo-C₁-C₃alkoxy, preferably unsubstituted or mono- or di-substituted by substituents selected from the group consisting of halogen and C₁-C₃alkyl;

(8) the basic ring structure of A is a pyridyl, 1-oxidopyridinio or thiazolyl group, the basic ring structure of A is preferably a pyrid-3-yl, 1-oxido-3-pyridinio or thiazol-5-yl group,

A is especially a pyrid-3-yl, 2-halopyrid-5-yl, 2,3-dihalopyrid-5-yl, 2-C₁-C₃alkylpyrid-5-yl, 1-oxido-3-pyridinio, 2-halo-1-oxido-5-pyridinio, 2,3-dihalo-1-oxido-5-pyridinio or 2-halo-thiazol-5-yl group,

A is more especially a pyrid-3-yl, 2-halopyrid-5-yl, 2-halo-1-oxido-5-pyridinio or 2-halothiazol-5-yl group,

A is preferably a 2-chloropyrid-5-yl, 2-methylpyrid-5-yl, 1-oxido-3-pyridinio, 2-chloro-1-oxido-5-pyridinio, 2,3-dichloro-1-oxido-5-pyridinio or 2-chlorothiazol-5-yl group,

A is more especially a pyrid-3-yl, 2-chloropyrid-5-yl, 2-chloro-1-oxido-5-pyridinio or 2-chlorothiazol-5-yl group,

A is especially a 2-chloropyrid-5-yl group or preferably a 2-chlorothiazol-5-yl group;

(9) R is C₁-C₆alkyl, phenyl-C₁-C₄alkyl, C₃-C₆cycloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl, especially C₁-C₆alkyl, C₃-C₆cycloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl,

preferably C₁-C₆alkyl, phenyl-C₁-C₄alkyl, C₃-C₄alkenyl or C₃-C₄alkynyl,

especially C₁-C₄alkyl, preferably methyl;

(10) X is N-NO₂;

(11) A is a pyridyl, 1-oxidopyridinio or thiazolyl group that is unsubstituted or mono- or di-substituted by substituents selected from the group consisting of halogen and C₁-C₃alkyl and is bonded to the remainder of compound I via a carbon atom of its basic ring structure; R is C₁-C₆alkyl, phenyl-C₁-C₄alkyl, C₃-C₆cycloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl and X is N-NO₂ or N-CN;

(12) A is a 2-chloropyrid-5-yl, 2-methylpyrid-5-yl, 1-oxido-3-pyridinio, 2-chloro-1-oxido-5-pyridinio, 2,3-dichloro-1-oxido-5-pyridinio or 2-chlorothiazol-5-yl group,

R is C₁-C₄alkyl and

X is N-NO₂; and

(13) A is a 2-chlorothiazol-5-yl or 2-chloropyrid-5-yl group,

R is C₁-C₄alkyl and

X is N-NO₂.

Among the compounds of formula (I), within the scope of the invention preference is given specifically to

(a) 5-(2-chloropyrid-5-ylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine,

(b) 5-(2-chlorothiazol-5-ylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine,

(c) 3-methyl-4-nitroimino-5-(1-oxido-3-pyridiniomethyl)-perhydro-1,3,5-oxadiazine,

(d) 5-(2-chloro-1-oxido-5-pyridiniomethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine
and

(e) 3-methyl-5-(2-methylpyrid-5-ylmethyl)-4-nitroimino-perhydro-1,3,5-oxadiazine.

The invention relates preferably to a composition that comprises a compound of formula (I) and either one or two of the following compounds:

cyproconazole, cyprodinil, difenoconazole, epoxiconazole, fenpicidonil, fludioxonil, flutriafol, furalaxyl, hymexazol, imazalil, metalaxyl (enantiomeric mixture), R-metalaxyl (D-form), penconazole, propiconazole, tebuconazole, tefluthrin, triazoxide or triticonazole.

Preference is given especially to a composition that comprises in addition to the compound of formula (I) only one microbicidal compound ,

especially to a composition that comprises a compound of formula (I) and fludioxonil, a compound of formula (I) and difenoconazol or a compound of formula (I) and R-metalaxyl;

above all to a composition that comprises the compound formula (Ia) and fludioxonil, the compound formula (Ia) and difenoconazol or the compound formula (Ia) and R-metalaxyl.

The compounds of formula (I) are known from EP-A-580 553.

Bitertanol is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 106;

cyproconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 268;

cyprodinil (CGA 219417) is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 161;

difenoconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 328;

diniconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 356;

epoxiconazole (BAS 480F) is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 67;

fenpiclonil is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 444;

fludioxonil is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 482;

fluquiconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 498;

flusilazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 510;

flutriafol is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 514;

furalaxyl is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 534;

hymexazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 576;

imazalil is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 580;

imibenconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 590;

ipconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 600;

metalaxyl is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 660; R-metalaxyl (D-form) is known from DE-P-25 15 091;

metconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 669;

pefurazoate is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 774;

penconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 776;

prochloraz is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 832;

propiconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 855;

SSF-109 is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 919;

tebuconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 942;

triazoxide is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 1009;

triadimefon is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 1000;

triadimenol is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 1001;

triflumizole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 1022;

triticonazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 1033; and

uniconazole is known from The Pesticide Manual, 10th Ed. (1994), The British Crop Protection Council, London, page 1034.

It has now been found, surprisingly, that the compositions according to the invention not only bring about the additive enhancement of the biocidal and physical properties of the individual active ingredients they contain that was in principle to be expected, but achieve a

synergistic effect which, *inter alia*, extends the boundaries of the pesticidal activity of the compounds.

In particular, it has now been found, surprisingly, that, for example, the pesticidal activity of the compositions according to the invention, compared with the pesticidal activity of the individual components, is not merely additive, as may essentially be expected, but that a synergistic effect exists. The term "synergistic" is not, however, in any way limited in this context to the pesticidal activity, but refers equally to other advantageous properties of the compositions according to the invention as compared with the individual components.

Examples of such advantageous properties that may be mentioned are: a broadening of the spectrum of pesticidal activity to other pests, for example to resistant strains, a reduction in the rate of application of the compounds of the formulae, adequate control of the pests with the aid of the compositions according to the invention, even at a rate of application at which the individual compounds are totally ineffective; advantageous behaviour during formulating and/or upon application, for example upon grinding, sieving, emulsifying, dissolving or dispersing; increased storage stability; improved stability to light; more advantageous degradability; improved toxicological and/or ecotoxicological behaviour, or other advantages familiar to a person skilled in the art.

In the area of pest control, the compositions according to the invention are valuable preventive and/or curative active ingredients having a very advantageous biocidal spectrum even at low rates of concentration, while being well tolerated by warm-blooded animals, fish and plants. The compositions of the invention are effective against all or individual development stages of normally sensitive animal pests, but also of resistant animal pests, such as insects and representatives of the order Acarina, and phytopathogenic fungi. The insecticidal and/or acaricidal action of the compositions of the invention may manifest itself directly, i.e. in the mortality of the pests, which occurs immediately or only after some time, for example during moulting, or indirectly, for example in reduced oviposition and/or a reduced hatching rate, the good activity corresponding to a mortality of at least 50 to 60 %.

The mentioned animal pests include, for example:

of the order Lepidoptera, for example,

Acleris spp., *Adoxophyes* spp., *Aegeria* spp., *Agrotis* spp., *Alabama argillaceae*, *Amylois* spp., *Anticarsia gemmatalis*, *Archips* spp., *Argyrotaenia* spp., *Autographa* spp., *Busseola fusca*, *Cadra cautella*, *Carposina nipponensis*, *Chilo* spp., *Choristoneura* spp., *Clysia ambiguella*, *Cnaphalocrocis* spp., *Cnephasia* spp., *Cochylis* spp., *Coleophora* spp., *Crocidolomia binotalis*, *Cryptophlebia leucotreta*, *Cydia* spp., *Diatraea* spp., *Diparopsis*

- 13 -

castanea, Earias spp., Ephestia spp., Eucosma spp., Eupoecilia ambiguella, Euproctis spp., Euxoa spp., Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula undalis, Hyphantria cunea, Keiferia lycopersicella, Leucoptera scitella, Lithocollethis spp., Lobesia botrana, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Operophtera spp., Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Pectinophora gossypiella, Phthorimaea operculella, Pieris rapae, Pieris spp., Plutella xylostella, Prays spp., Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp., Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni and Yponomeuta spp.;

of the order Coleoptera, for example,

Agriotes spp., Anthonomus spp., Atomaria linearis, Chaetocnema tibialis, Cosmopolites spp., Curculio spp., Dermestes spp., Diabrotica spp., Epilachna spp., Eremnus spp., Leptinotarsa decemlineata, Lissorhoptrus spp., Melolontha spp., Orycaephilus spp., Otiorhynchus spp., Phlyctinus spp., Popillia spp., Psylliodes spp., Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Tenebrio spp., Tribolium spp. and Trogoderma spp.;

of the order Orthoptera, for example,

Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Periplaneta spp. and Schistocerca spp.;

of the order Isoptera, for example,

Reticulitermes spp.;

of the order Psocoptera, for example,

Liposcelis spp.;

of the order Anoplura, for example,

Haematopinus spp., Linognathus spp., Pediculus spp., Pemphigus spp. and Phylloxera spp.;

of the order Mallophaga, for example,

Damalinea spp. and Trichodectes spp.;

of the order Thysanoptera, for example,

Frankliniella spp., Hercinothrips spp., Taeniothrips spp., Thrips palmi, Thrips tabaci and Scirtothrips aurantii;

- 14 -

of the order Heteroptera, for example,

Cimex spp., *Distantiella theobroma*, *Dysdercus* spp., *Euchistus* spp., *Eurygaster* spp.,
Leptocoris spp., *Nezara* spp., *Piesma* spp., *Rhodnius* spp., *Sahlbergella singularis*,
Scotinophara spp. and *Triatoma* spp.;

of the order Homoptera, for example,

Aleurothrixus floccosus, *Aleyrodes brassicae*, *Aonidiella* spp., Aphididae, *Aphis* spp.,
Aspidiotus spp., *Bemisia tabaci*, *Ceroplaster* spp., *Chrysomphalus aonidium*,
Chrysomphalus dictyospermi, *Coccus hesperidum*, *Empoasca* spp., *Eriosoma larigerum*,
Erythroneura spp., *Gascardia* spp., *Laodelphax* spp., *Lecanium corni*, *Lepidosaphes* spp.,
Macrosiphus spp., *Myzus* spp., *Nephotettix* spp., *Nilaparvata* spp., *Paratoria* spp.,
Pemphigus spp., *Planococcus* spp., *Pseudaulacaspis* spp., *Pseudococcus* spp., *Psylla*
spp., *Pulvinaria aethiopica*, *Quadraspidotus* spp., *Rhopalosiphum* spp., *Saissetia* spp.,
Scaphoideus spp., *Schizaphis* spp., *Sitobion* spp., *Trialeurodes vaporariorum*, *Trioza*
erytreae and *Unaspis citri*;

of the order Hymenoptera, for example,

Acromyrmex, *Atta* spp., *Cephus* spp., *Diprion* spp., *Diprionidae*, *Gilpinia polytoma*,
Hoplocampa spp., *Lasius* spp., *Monomorium pharaonis*, *Neodiprion* spp., *Solenopsis* spp.
and *Vespa* spp.;

of the order Diptera, for example,

Aedes spp., *Antherigona soccata*, *Bibio hortulanus*, *Calliphora erythrocephala*, *Ceratitis*
spp., *Chrysomyia* spp., *Culex* spp., *Cuterebra* spp., *Dacus* spp., *Drosophila melanogaster*,
Fannia spp., *Gastrophilus* spp., *Glossina* spp., *Hypoderma* spp., *Hyppobosca* spp.,
Liriomyza spp., *Lucilia* spp., *Melanagromyza* spp., *Musca* spp., *Oestrus* spp., *Orseolia* spp.,
Oscinella frit, *Pegomyia hyoscyami*, *Phorbia* spp., *Rhagoletis pomonella*, *Sciara* spp.,
Stomoxys spp., *Tabanus* spp., *Tannia* spp. and *Tipula* spp.;

of the order Siphonaptera, for example,

Ceratophyllus spp. and *Xenopsylla cheopis*;

of the order Thysanura, for example,

Lepisma saccharina;

of the order Acarina, for example,

Acarus siro, *Aceria sheldoni*, *Aculus schlechtendali*, *Amblyomma* spp., *Argas* spp.,
Boophilus spp., *Brevipalpus* spp., *Bryobia praetiosa*, *Calipitimerus* spp., *Chorioptes* spp.,

Dermanyssus gallinae, *Eotetranychus carpini*, *Eriophyes* spp., *Hyalomma* spp., *Ixodes* spp., *Olygonychus pratensis*, *Omithodoros* spp., *Panonychus* spp., *Phyllocoptuta oleivora*, *Polyphagotarsonemus latus*, *Psoroptes* spp., *Rhipicephalus* spp., *Rhizoglyphus* spp., *Sarcoptes* spp., *Tarsonemus* spp. and *Tetranychus* spp..

The mentioned phytopathogenic fungi include, for example:

of the class of the Fungi imperfecti, for example,

Botrytis spp., *Pyricularia* spp., *Helminthosporium* spp., *Fusarium* spp., *Septoria* spp., *Cercospora* spp. and *Alternaria* spp.;

of the class of the Basidiomycetes, for example,

Rhizoctonia spp., *Hemileia* spp. and *Puccinia* spp.;

of the class of the Ascomycetes, for example,

Venturia spp., *Erysiphe* spp., *Podosphaera* spp., *Monilinia* spp. and *Uncinula* spp.; and

of the class of the Oomycetes, for example,

Phytophthora spp., *Pythium* spp. and *Plasmopara* spp..

With the compositions according to the invention it is possible especially to control, i.e. to inhibit or destroy, pests of the mentioned type occurring on plants, especially on useful plants and ornamentals in agriculture, in horticulture and in forestry, or on parts of such plants, such as the fruit, blossom, leaves, stems, tubers or roots, while in some cases the parts of the plants which grow later are also still protected against those pests.

Target crops are especially cereals, such as wheat, barley, rye, oats, rice, maize and sorghum; beet, such as sugar beet and fodder beet; fruit, such as pomes, stone fruit and soft fruit, such as apples, pears, plums, peaches, almonds, cherries, or berries, for example strawberries, raspberries or blackberries; leguminous plants, such as beans, lentils, peas and soybeans; oil plants, such as rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans and groundnuts; cucumber plants, such as marrows, cucumbers and melons; fibre plants, such as cotton, flax, hemp and jute; citrus fruit, such as oranges, lemons, grapefruit and mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes and paprika; lauraceae, such as avocados, cinnamon and camphor; and tobacco, nuts, coffee, aubergines, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals. Preference is given especially to the control of pests and microorganisms on wheat, barley, rape, maize and sugar beet.

The compositions of the invention are suitable especially for controlling insects and representatives of the order Acarina, especially plant-destructive feeding insects, such as *Anthonomus grandis*, *Diabrotica balteata*, *Heliothis virescens* larvae, *Plutella xylostella* and *Spodoptera littoralis* larvae, and spider mites, such as *Tetranychus* spp., in cotton, fruit, maize, soybean, rape and vegetable crops.

Further areas of use of the compounds according to the invention are the protection of stored goods and stocks and materials, and also in the hygiene sector, especially the protection of domestic animals and productive livestock against pests of the mentioned type.

The composition according to the invention is therefore an emulsifiable concentrate, a suspension concentrate, a directly sprayable or dilutable solution, a coatable paste, a dilute emulsion, a wettable powder, a soluble powder, a dispersible powder, a wettable powder, a dust, granules or an encapsulation in polymer substances, comprising in addition to the compound of formula (I), and where appropriate at least one further insecticidally active compound, at least one fungicidally active compound, the type of formulation being chosen in accordance with the intended objectives and prevailing circumstances.

The active ingredients are used in those compositions in pure form, a solid active ingredient, for example, in a specific particle size, or preferably together with - at least - one of the adjuvants customary in formulation technology, such as extenders, for example solvents or solid carriers, or surface-active compounds (surfactants).

Suitable solvents are, for example: optionally partially hydrogenated aromatic hydrocarbons, preferably the fractions of alkylbenzenes containing 8 to 12 carbon atoms, such as xylene mixtures, alkylated naphthalenes or tetrahydronaphthalene, aliphatic or cycloaliphatic hydrocarbons, such as paraffins or cyclohexane, alcohols, such as ethanol, propanol or butanol, glycols and their ethers and esters, such as propylene glycol, dipropylene glycol ether, ethylene glycol or ethylene glycol monomethyl or monoethyl ether, ketones, such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents, such as N-methylpyrrolid-2-one, dimethyl sulfoxide or N,N-dimethylformamide, water, vegetable oils or epoxidised vegetable oils, such as rape oil, castor oil, coconut oil or soybean oil or epoxidised rape oil, castor oil, coconut oil or soybean oil, and silicone oils.

The solid carriers used, e.g. for dusts and dispersible powders, are normally natural mineral fillers such as calcite, talcum, kaolin, montmorillonite or attapulgite. In order to improve the physical properties it is also possible to add highly dispersed silicic acids or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types, such as

pumice, broken brick, sepiolite or bentonite; and suitable nonsorbent carriers are calcite or sand. In addition, a great number of granulated materials of inorganic or organic nature can be used, especially dolomite or pulverised plant residues.

Depending on the nature of the compound to be formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants or mixtures of surfactants having good emulsifying, dispersing and wetting properties. The surfactants listed below are to be regarded merely as examples; many more surfactants customarily employed in formulation technology and suitable for use according to the invention are described in the relevant literature.

Non-ionic surfactants are preferably polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, said derivatives containing 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety and 6 to 18 carbon atoms in the alkyl moiety of the alkylphenols. Further suitable non-ionic surfactants are water-soluble adducts of polyethylene oxide with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol containing 1 to 10 carbon atoms in the alkyl chain, which adducts contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. These compounds usually contain 1 to 5 ethylene glycol units per propylene glycol unit. Representative examples of non-ionic surfactants are nonylphenol polyethoxyethanols, castor oil polyglycol ethers, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol. Fatty acid esters of polyoxyethylene sorbitan, e.g. polyoxyethylene sorbitan trioleate, are also suitable non-ionic surfactants.

Cationic surfactants are preferably quaternary ammonium salts which contain, as substituent, at least one C_8 - C_{22} alkyl radical and, as further substituents, unsubstituted or halogenated lower alkyl, benzyl or hydroxy-lower alkyl radicals. The salts are preferably in the form of halides, methyl sulfates or ethyl sulfates. Examples are stearyltrimethylammonium chloride and benzyldi(2-chloroethyl)ethylammonium bromide.

Both water-soluble soaps and water-soluble synthetic surface-active compounds are suitable anionic surfactants. Suitable soaps are the alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts of higher fatty acids (C_{10} - C_{22}), e.g. the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which can be obtained e.g. from coconut oil or tall oil; mention may also be made of fatty acid methyltaurine salts. More frequently, however, so-called synthetic surfactants are used, especially fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates. The fatty sulfonates or sulfates are usually in the form of alkali metal salts, alkaline earth

metal salts or unsubstituted or substituted ammonium salts and generally contain a C_8 - C_{22} -alkyl radical, which also includes the alkyl moiety of acyl radicals; there may be mentioned by way of example the sodium or calcium salt of lignosulfonic acid, of dodecyl sulfate or of a mixture of fatty alcohol sulfates obtained from natural fatty acids. These compounds also comprise the salts of sulfated and sulfonated fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonic acid groups and one fatty acid radical containing approximately 8 to 22 carbon atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolammonium salts of dodecylbenzenesulfonic acid, dibutynaphthalenesulfonic acid or of a condensate of naphthalenesulfonic acid and formaldehyde. Also suitable are corresponding phosphates, e.g. salts of the phosphoric acid ester of an adduct of p-nonylphenol with 4 to 14 mol of ethylene oxide, or phospholipids.

The compositions usually comprise 0.1 to 99%, preferably 0.1 to 95%, of active ingredient mixture, and 1 to 99.9%, preferably 5 to 99.9%, of - at least - one solid or liquid adjuvant, it generally being possible for 0 to 25%, preferably 0.1 to 20%, of the composition to be surfactants (in each case percentages are by weight). Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations which have considerably lower active ingredient concentrations. Preferred compositions are especially the following (throughout, percentages are by weight):

The active ingredient combinations according to the invention preferably comprise a compound of formula (I) and two compounds selected from the compounds of formulae (II) to (V) in a mixing ratio of from 1 (compound of formula I) : 1 (compound of formulae (II) to (V)) : 100 (compound of formulae (II) to (V)), 1:100:1 to 100:1:1, especially from 1:1:20, 1:20:1 to 20:1:1, more especially from 1:1:10, 1:10:1 to 10:1:1, especially from 1:1:5, 1:5:1 to 5:1:1, very especially from 1:1:2, 1:2:1 to 2:1:1, and above all 1:1:1; 1:1:2; 1:2:1; 2:1:1; 1:1:3; 1:3:1; 3:1:1; 1:1:4; 1:4:1; 4:1:1; 7:1:1; 35:5:1; 35:5:3; 35:2.5:1; 52.5:3.75:1.5; 35:5:1; 52.5:5:2; 52.5:5:3; 52.5:5:7.5; 52.5:5:1; 52.5:5:3; 52.5:2:2; 420:50:12; 315:1:2.5; 15:4:18 to 7 : 4 : 1.

On the other hand, preference is given also to active ingredient combinations comprising a compound I, a pyrethroid and two compounds of formulae (II) to (V), especially in the ratio of 7:4:1:1.

Preference is given likewise to an active ingredient combination comprising a compound of formula (I) and only one compound selected from the compounds of formulae (II) to (V) in a mixing ratio of from 1:50 to 50:1, especially in a ratio of from 1:20 to 20:1, especially from 10:1 to 1:10, very especially from 5:1 to 1:5, preferably from 2:1 to 1:2, above all in the ratio

of 1:1; or else in the ratio of 7:1, 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 3:4, or 1:3, or 2:3, or 1:2.

Preference is given furthermore to an active ingredient combination comprising

1. a compound of formula (I), especially of formula (Ia), fludioxonil and difenoconazole;
2. a compound of formula (I), especially of formula (Ia), fludioxonil and tebuconazole;
3. a compound of formula (I), especially of formula (Ia), fludioxonil and triticonazole;
4. a compound of formula (I), especially of formula (Ia), fludioxonil and penconazole;
5. a compound of formula (I), especially of formula (Ia), fludioxonil and epoxiconazole;
6. a compound of formula (I), especially of formula (Ia), fludioxonil and cyproconazole;
7. a compound of formula (I), especially of formula (Ia), and fludioxonil;
8. a compound of formula (I), especially of formula (Ia), cyprodinil and tebuconazole;
9. a compound of formula (I), especially of formula (Ia), cyprodinil and epoxiconazole;
10. a compound of formula (I), especially of formula (Ia), cyprodinil and flutriafol;
11. a compound of formula (I), especially of formula (Ia), cyprodinil and cyproconazole;
12. a compound of formula (I), especially of formula (Ia), cyprodinil and triticonazole;
13. a compound of formula (I), especially of formula (Ia), triazoxide and tebuconazole;
14. a compound of formula (I), especially of formula (Ia), R-metalaxyl and fludioxonil;
15. a compound of formula (I), especially of formula (Ia), R-metalaxyl and fludioxonil;
16. a compound of formula (I), especially of formula (Ia), tefluthrin and hymexazol;
17. a compound of formula (I), especially of formula (Ia), tefluthrin and fludioxonil; and
18. a compound of formula (I), especially of formula (Ia), tefluthrin, fludioxonil and difenoconazole.

Preference is given especially to an active ingredient combination comprising

- A1) the compound of formula (Ia), fludioxonil and difenoconazole in a mixing ratio of 7 : 1 : 1;
- A2) the compound of formula (Ia), fludioxonil and tebuconazole in a mixing ratio of 35 : 5 : 1;
- A3) the compound of formula (Ia), fludioxonil and triticonazole in a mixing ratio of 35 : 5 : 3;
- A4) the compound of formula (Ia), fludioxonil and epoxiconazole in a mixing ratio of 35 : 2.5 : 1;
- A5) the compound of formula (Ia), fludioxonil and epoxiconazole in a mixing ratio of 52.5 : 3.75 : 1.5;
- A6) the compound of formula (Ia), fludioxonil and cyproconazole in a mixing ratio of 35 : 5 : 1;

- A7) the compound of formula (Ia) and fludioxonil in a mixing ratio of 7 : 1;
- A8) the compound of formula (Ia), cyprodinil and tebuconazole in a mixing ratio of 52.5 : 5 : 2;
- A9) the compound of formula (Ia), cyprodinil and epoxiconazole in a mixing ratio of 52.5 : 5 : 3;
- A10) the compound of formula (Ia), cyprodinil and flutriafol in a mixing ratio of 52.5 : 5 : 7.5;
- A11) the compound of formula (Ia), cyprodinil and cyproconazole in a mixing ratio of 52.5 : 5 : 1;
- A12) the compound of formula (Ia), cyprodinil and triticonazole in a mixing ratio of 52.5 : 5 : 3;
- A13) the compound of formula (Ia), triazoxide and tebuconazole in a mixing ratio of 52.5 : 2 : 2;
- A14) the compound of formula (Ia), R-metalaxyl and fludioxonil in a mixing ratio of 420 : 50 : 12;
- A15) the compound of formula (Ia), R-metalaxyl and fludioxonil in a mixing ratio of 315 : 1 : 2.5;
- A16) the compound of formula (Ia), tefluthrin and hymexazol in a mixing ratio of 15 : 4 : 18;
- A17) the compound of formula (Ia), tefluthrin and fludioxonil in a mixing ratio of 7 : 4 : 1; and
- A18) the compound of formula (Ia), tefluthrin, fludioxonil and difenoconazole in a mixing ratio of 7 : 4 : 1 : 1.

The above-mentioned mixing ratios relate on the one hand to parts by weight of the individual components, but on the other hand also to the mixing ratios in moles. Thus, for example, the ratio of 4 : 1 : 1 denotes four parts by weight of a compound of formula (I) to one part by weight of a fungicidal compound to one part by weight of a further fungicidally or insecticidally active compound, but also four moles of a compound of formula (I) to one mole of a fungicidal compound to one mole of a further fungicidally or insecticidally active compound. Finally, the figures relate also to mixtures in the ratio of the LD₅₀ values of the individual pests to be controlled.

Emulsifiable concentrates:

insecticidally active compounds	1 to 90%, preferably 5 to 20%
compounds (II) to (V)	1 to 90%, preferably 5 to 20%
surfactant:	1 to 30%, preferably 15 to 20%
solvent:	to 98%, preferably 70 to 85%

- 21 -

Dusts:

insecticidally active compounds	0.1 to 10%, preferably 0.1 to 1%
compounds (II) to (V)	0.1 to 10%, preferably 0.1 to 1%
solid carrier:	99.9 to 90%, preferably 99.9 to 99%

Suspension concentrates:

insecticidally active compounds	5 to 75%, preferably 10 to 50%
compounds (II) to (V)	5 to 75%, preferably 10 to 50%
water:	94 to 24%, preferably 88 to 30%
surfactant:	1 to 40%, preferably 2 to 30%

Wettable powders:

insecticidally active compounds	0.5 to 90%, preferably 1 to 80%
compounds (II) to (V)	0.5 to 90%, preferably 1 to 80%
surfactant:	0.5 to 20%, preferably 1 to 15%
solid carrier:	5 to 99%, preferably 15 to 98%

Granules:

insecticidally active compounds	0.5 to 30%, preferably 3 to 15%
solid carrier:	99.5 to 70%, preferably 97 to 85%

The compositions according to the invention may also comprise further solid or liquid adjuvants, such as stabilisers, for example vegetable oils or epoxidised vegetable oils (e.g. epoxidised coconut oil, rape oil or soybean oil), antifoams, for example silicone oil, preservatives, viscosity regulators, binders and/or tackifiers, as well as fertilisers or other active ingredients for obtaining special effects, for example bactericides, nematicides, molluscicides or selective herbicides.

The compositions according to the invention are prepared in known manner, in the absence of adjuvants, for example by grinding and/or sieving a solid active ingredient or mixture of active ingredients, for example to a specific particle size, and in the presence of at least one adjuvant, for example by intimately mixing and/or grinding the active ingredient or mixture of active ingredients with the adjuvant(s). The invention relates also to those processes for the preparation of the compositions according to the invention and to the use of the compounds of formula (I) in the preparation of those compositions.

The invention relates also to the methods of application of the compositions, i.e. the methods of controlling pests and microorganisms of the mentioned type, such as spraying, atomising, dusting, coating, dressing, scattering or pouring, which are selected in accordance with the intended objectives and prevailing circumstances, and to the use of the compositions for controlling pests of the mentioned type. Typical rates of concentration are from 0.1 to 1000 ppm, preferably from 0.1 to 500 ppm, of active ingredient. The rates of application per hectare are generally from 1 to 2000 g of active ingredient per hectare, especially from 10 to 1000 g/ha, preferably from 20 to 600 g/ha.

A preferred method of application in the area of plant protection is application to the foliage of the plants (foliar application), the number of applications and the rate of application depending on the risk of infestation by the pest in question. However, the active ingredient can also penetrate the plants through the roots (systemic action) if the locus of the plants is impregnated with a liquid formulation or if the active ingredient is incorporated in solid form into the locus of the plants, for example into the soil, e.g. in granular form (soil application). In paddy rice crops, such granules may be applied in metered amounts to the flooded rice field.

The compositions according to the invention are also suitable for protecting plant propagation material, e.g. seed material, such as fruit, tubers or grains, or plant cuttings, from fungal infections and animal pests. The propagation material can be treated with the composition before planting: seed, for example, can be dressed before being sown. The compounds of the invention can also be applied to grains (coating), either by impregnating the grains with a liquid formulation or by coating them with a solid formulation. The composition can also be applied to the planting site when the propagation material is being planted, for example to the seed furrow during sowing. The invention relates also to that method of treating plant propagation material and to the plant propagation material thus treated.

- 23 -

<u>Example F1: Emulsifiable concentrates</u>	a)	b)	c)
pesitically active compounds	25%	40%	50%
calcium dodecylbenzenesulfonate	5%	8%	6%
castor oil polyethylene glycol ether (36 mol EO)	5%	-	-
tributylphenol polyethylene glycol ether (30 mol EO)	-	12%	4%
cyclohexanone	-	15%	20%
xylene mixture	65%	25%	20%

Such concentrates can be diluted with water to give emulsions of any desired concentration.

<u>Example F2: Solutions</u>	a)	b)	c)	d)
pesitically active compounds	80%	10%	5%	95%
ethylene glycol monomethyl ether	20%	-	-	-
polyethylene glycol (mol. wt. 400)	-	70%	-	-
N-methylpyrrolid-2-one	-	20%	-	-
epoxidised coconut oil	-	-	1%	5%
petroleum fraction (boiling range: 160-190°C)	-	-	94%	-

The solutions are suitable for use in the form of microdrops.

<u>Example F3: Granules</u>	a)	b)	c)	d)
pesitically active compounds	5%	10%	8%	21%
kaolin	94%	-	79%	54%
highly dispersed silicic acid	1%	-	13%	7%
attapulgit	-	90%	-	18%

The active ingredients are dissolved in dichloromethane and the solution is sprayed onto the carrier and the solvent is then evaporated off *in vacuo*.

<u>Example F4: Dusts</u>	a)	b)
pesitically active compounds	2%	5%
highly dispersed silicic acid	1%	5%
talcum	97%	-
kaolin	-	90%

The active ingredient is homogeneously mixed with the carriers, giving dusts that are ready for use.

Example F5: Wettable powders

	a)	b)	c)
pesticidally active compounds	25%	50%	75%
sodium lignosulfonate	5%	5%	-
sodium laurylsulfate	3%	-	5%
sodium diisobutyl-naphthalenesulfonate	-	6%	10%
octylphenol polyethylene glycol ether (7-8 mol EO)	-	2%	-
highly dispersed silicic acid	5%	10%	10%
kaolin	62%	27%	-

The active ingredient is mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of the desired concentration.

Example F6: Emulsifiable concentrate

pesticidally active compounds	10%
octylphenol polyethylene glycol ether (4-5 mol EO)	3%
calcium dodecylbenzenesulfonate	3%
castor oil polyethylene glycol ether (36 mol EO)	4%
cyclohexanone	30%
xylene mixture	50%

This concentrate can be diluted with water to give emulsions of any desired concentration.

Example F7: Dusts

	a)	b)
pesticidally active compounds	5%	8%
talcum	95%	-
kaolin	-	92%

Ready-for-use dusts are obtained by mixing the active ingredient with the carrier and grinding the mixture in a suitable mill.

Example F8: Extruder granules

pesticidally active compounds	10%
sodium lignosulfonate	2%
carboxymethylcellulose	1%
kaolin	87%

The active ingredient is mixed with the adjuvants and the mixture is ground and moistened with water. The mixture is extruded and granulated and the granules are dried in a stream of air.

Example F9: Coated granules

pesticidally active compounds	3%
polyethylene glycol (mol. wt. 200)	3%
kaolin	94%

The finely ground active ingredient is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

Example F10: Suspension concentrate

pesticidally active compounds	40%
ethylene glycol	10%
nonylphenol polyethylene glycol ether (15 mol EO)	6%
sodium lignosulfonate	10%
carboxymethylcellulose	1%
aqueous formaldehyde solution (37%)	0.2%
aqueous silicone oil emulsion (75%)	0.8%
water	32%

The finely ground active ingredient is homogeneously mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

Biological Examples (throughout, percentages are by weight, unless otherwise indicated)

Example B1: Action against Boophilus microplus

Adult female ticks which are replete with blood are affixed to a PVC plate and covered with a cotton wool swab. For treatment, 10 ml of an aqueous test solution containing 125 ppm of the test compound mixture are poured over the test insects. The cotton wool swab is then removed and the ticks are incubated for 4 weeks until oviposition has taken place. The action against *Boophilus microplus* manifests itself either as mortality or sterility of the females or as ovicidal action in the eggs.

The compositions according to the invention exhibit good activity in this test.

Example B2: Action against Nilaparvata lugens

Rice plants are sprayed with an aqueous emulsion comprising 400 ppm of the test compound mixture. After the spray coating has dried, the rice plants are populated with cicada larvae in the 2nd and 3rd stages. Evaluation is made 21 days later. The percentage reduction in the population (% activity) is determined by comparing the number of surviving cicadas on the treated plants with that on untreated plants.

The compositions according to the invention exhibit good activity in this test. In particular, a composition comprising the compound of formula (Ia), fludioxonil and difenoconazole in a mixing ratio of 7 : 1 : 1 is more than 80 % effective.

Example B3: Action against Diabrotica balteata larvae

Maize seedlings are sprayed with an aqueous emulsion comprising 400 ppm of the test compound mixture. After the spray coating has dried, the maize seedlings are populated with 10 Diabrotica balteata larvae in the second stage and placed in a plastics container. Evaluation is made 6 days later. The percentage reduction in the population (% activity) is determined by comparing the number of dead larvae on the treated plants with that on untreated plants.

The compositions according to the invention exhibit good activity in this test. In particular, a composition comprising the compound of formula (Ia), R-metalaxyl and fludioxonil in a mixing ratio of 315 : 1 : 2.5 is more than 80 % effective.

Example B4: Action against Anthonomus grandis adults

Young cotton plants are sprayed with an aqueous emulsion comprising 400 ppm of the test compound mixture. After the spray coating has dried, the cotton plants are populated with 10 Anthonomus grandis adults and placed in a plastics container. Evaluation is made 3 days later. The percentage reduction in the population or the percentage reduction in feeding damage (% activity) is determined by comparing the number of dead beetles and the feeding damage on the treated plants with that on untreated plants.

The compositions according to the invention exhibit good activity in this test. In particular, a composition comprising the compound of formula (Ia), fludioxonil and tebuconazole in a mixing ratio of 35 : 5 : 1 is more than 80 % effective.

Example B5: Action against *Heliothis virescens* caterpillars

Young soybean plants are sprayed with an aqueous emulsion comprising 400 ppm of the test compound mixture. After the spray coating has dried, the soybean plants are populated with 10 *Heliothis virescens* caterpillars in the first stage and placed in a plastics container. Evaluation is made 6 days later. The percentage reduction in the population or the percentage reduction in feeding damage (% activity) is determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on untreated plants.

The compositions according to the invention exhibit good activity in this test. In particular, a composition comprising the compound of formula (Ia), fludioxonil and tebuconazole, especially in a mixing ratio of 35 : 5 : 1; is more than 80 % effective.

Example B6: Action against *Spodoptera littoralis* caterpillars

Young soybean plants are sprayed with an aqueous emulsion comprising 400 ppm of the test compound mixture. After the spray coating has dried, the soybean plants are populated with 10 *Spodoptera littoralis* caterpillars in the third stage and placed in a plastics container. Evaluation is made 3 days later. The percentage reduction in the population or the percentage reduction in feeding damage (% activity) is determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on untreated plants.

The compositions according to the invention exhibit good activity in this test. In particular, a composition comprising the compound of formula (Ia), fludioxonil and tebuconazole in a mixing ratio of 35 : 5 : 1 is more than 80 % effective.

Example B7: Action against *Crocidolomia binotalis* caterpillars

Young cabbage plants are sprayed with an aqueous emulsion comprising 400 ppm of the test compound mixture. After the spray coating has dried, the cabbage plants are populated with 10 *Crocidolomia binotalis* caterpillars in the third stage and placed in a plastics container. Evaluation is made 3 days later. The percentage reduction in the population or the percentage reduction in feeding damage (% activity) is determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on untreated plants.

The compositions according to the invention exhibit good activity in this test.

Example B8: Systemic action against Nilaparvata lugens

Pots containing rice plants are placed in an aqueous emulsion solution containing 400 ppm of the test compound mixture. The rice plants are then populated with larvae in the 2nd and 3rd stages. Evaluation is made 6 days later. The percentage reduction in the population (% activity) is determined by comparing the number of cicadas on the treated plants with that on untreated plants.

The compositions according to the invention exhibit good activity in this test.

Example B9: Ovicidal action against Tetranychus urticae

Young bean plants are populated with Tetranychus urticae females which are removed 24 hours later. The plants populated with eggs are sprayed with an aqueous emulsion comprising 400 ppm of the test compound mixture. The plants are then incubated for 6 days at 25°C and then evaluated. The percentage reduction in the population (% activity) is determined by comparing the number of dead eggs, larvae and adults on the treated plants with that on untreated plants.

The compositions according to the invention exhibit good activity in this test. In particular, a composition comprising the compound of formula (Ia), cyprodinil and flutriafol in a mixing ratio of 52.5 : 5 : 7.5 is more than 80 % effective.

Example B10: Action against Dermanyssus gallinae

2 to 3 ml of a solution comprising 10 ppm of the test compound mixture, and approximately 200 mites at various stages of development, are placed in a glass container that is open at the top. The container is then closed with a cotton wool plug, shaken for 10 minutes until the mites are completely wetted, and then inverted for a short time so that the remaining test solution can be absorbed by the cotton wool. After 3 days, the percentage mortality of the mites is determined by counting the dead individuals.

The compositions according to the invention exhibit good activity in this test. In particular, a composition comprising the compound of formula (Ia), tefluthrin, fludioxonil and difenoconazole in a mixing ratio of 7 : 4 : 1 : 1 is more than 80 % effective.

Example B11: Action against Blattella germanica

An amount of 0.1 % solution of the test compound mixture in acetone corresponding to a rate of concentration of 2 g/m² is introduced into a petri dish. When the solvent has evaporated, 20 Blattella germanica nymphs (final nymph stage) are introduced into the

prepared dish and exposed to the action of the test compound for 2 hours. The nymphs are then anaesthetised with CO₂, placed in a fresh petri dish and kept in the dark at 25°C and 50 to 70 % humidity. After 48 hours the insecticidal activity is determined by establishing the mortality.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A1 to A18 are more than 80 % effective.

Example B12: Action against *Lucilia cuprina* blowflies

Freshly laid eggs of the blowfly variety *Lucilia cuprina* are introduced in small portions (30 to 50 eggs) into test tubes in which 4 ml of nutrient medium and 1 ml of test solution comprising 16 ppm of the test compound mixture have already been mixed. After inoculation of the culture medium, the test tubes are closed with a cotton wool plug and incubated in an incubating cabinet for 4 days at 30°C. By that time, larvae approximately 1 cm long (stage 3) have developed in the untreated medium. If the substance is active, the larvae are either dead or severely retarded by that time. Evaluation is carried out after 96 hours.

The compositions according to the invention exhibit good activity in this test. In particular, a composition comprising the compound of formula (Ia), fludioxonil and difenoconazole in a mixing ratio of 7 : 1 : 1 is more than 80 % effective.

Example B13: Action against *Musca domestica*

A sugar cube is treated with a solution of the test compound mixture in such a manner that after drying overnight the concentration of test compound in the sugar is 250 ppm. The treated sugar cube, together with a wet cotton wool swab and 10 *Musca domestica* adults of an OP-resistant strain, is placed in an aluminium dish, covered with a glass beaker and incubated at 25°C. After 24 hours the mortality is determined.

The compositions according to the invention exhibit good activity in this test. In particular, a composition comprising the compound of formula (Ia), triazoxide and tebuconazole in a mixing ratio of 52.5 : 2 : 2 is more than 80 % effective.

Example B14: Action against *Plutella xylostella* caterpillars

Young cabbage plants are sprayed with an aqueous emulsion comprising 400 ppm of the test compound mixture. After the spray coating has dried, the cabbage plants are populated with 10 *Plutella xylostella* caterpillars in the third stage and placed in a plastics container. Evaluation is made 3 days later. The percentage reduction in the population or

the percentage reduction in feeding damage (% activity) is determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with that on untreated plants.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A1, A3, A7 and A13 effect almost complete inhibition of infestation.

Example B15: Action against Phytophthora infestans on tomatoes

a) Curative action

After a cultivation period of 3 weeks, tomato plants of the "Red Gnome" variety are sprayed with a zoospore suspension of the fungus and incubated in a cabinet at 18 to 20°C and 100 % humidity. Humidification is stopped after 24 hours. When the plants have dried, they are sprayed with a mixture comprising the test compound mixture formulated as a wettable powder in a concentration of 200 ppm. After the spray coating has dried, the plants are again placed in the humidity cabinet for 4 days. The activity of the test compounds is evaluated on the basis of the number and size of the typical leaf specks that have occurred after that time.

b) Preventive-systemic action

The test compound mixture formulated as a wettable powder is applied in a concentration of 60 ppm (based on the volume of the soil) to the soil surface of three-week-old tomato plants of the "Red Gnome" variety planted in pots. After a 3-day waiting period, the undersides of the leaves of the plants are sprayed with a zoospore suspension of *Phytophthora infestans*. The plants are then kept in a spray cabinet for 5 days at 18 to 20°C and 100 % humidity. After that time, typical leaf specks form, the number and size of which are used to evaluate the activity of the test compounds.

Whereas untreated but infected control plants exhibit 100 % infestation, good activity is achieved with the compositions according to the invention. In particular, compound mixtures A1 to A18 inhibit infestation in both tests to 20 % or less.

Example B16: Action against Plasmopara viticola (Bert. et Curt.) (Bert. et DeToni) on vines

a) Residual-preventive action

Vine seedlings of the "Chasselas" variety are grown in a greenhouse. 3 plants are sprayed at the 10-leaf stage with a mixture (200 ppm active ingredient mixture). After the spray

coating has dried, the undersides of the leaves of the plants are infected uniformly with a spore suspension of the fungus. The plants are then kept in a humidity chamber for 8 days. After that time, the control plants exhibit marked symptoms of disease. The activity of the test compounds is evaluated on the basis of the number and size of the sites of infection on the treated plants.

b) Curative action

Vine seedlings of the "Chasselas" variety are grown in a greenhouse and the undersides of the leaves are infected at the 10-leaf stage with a spore suspension of *Plasmopara viticola*. After 24 hours in a humidity cabinet, the plants are sprayed with a mixture of the test compounds (200 ppm, 60 ppm, 20 ppm active ingredient mixture). Then the plants are kept in the humidity cabinet for a further 7 days. After that time, the control plants exhibit symptoms of disease. The activity of the test compounds is evaluated on the basis of the number and size of the sites of infection on the treated plants.

The compositions according to the invention exhibit good activity in this test. In comparison with the control plants, infestation is 20 % or less, especially on the plants treated with compound mixtures A1 to A18.

Example B17: Action against *Pythium debaryanum* on sugar beet (*Beta vulgaris*)

a) Action following soil application

The fungus is cultivated on sterile oat grains and added to a soil/sand mixture. The soil so infected is introduced into plant pots and sown with sugar beet seeds. Immediately after sowing, the test compounds, formulated as wettable powders, are poured in the form of an aqueous suspension over the soil (20 ppm active ingredient mixture, based on the volume of the soil). The pots are then placed in a greenhouse at 20-24°C for 2-3 weeks. The soil is kept uniformly moist by light spraying with water. The test is evaluated by determining the emergence of the sugar beet plants and the proportion of healthy and diseased plants.

b) Action following application by dressing

The fungus is cultivated on sterile oat grains and added to a soil/sand mixture. The soil so infected is introduced into plant pots and sown with sugar beet seeds which have been dressed with the test compounds formulated as dressing powders (1000 ppm active ingredient mixture, based on the weight of the seeds). The pots containing the seeds are

then placed in a greenhouse at 20-24°C for 2-3 weeks. The soil is kept uniformly moist by light spraying with water.

The test is evaluated by determining the emergence of the sugar beet plants and the proportion of healthy and diseased plants.

The compositions according to the invention exhibit good activity in this test. In particular, after treatment with compound mixtures A1 to A18 more than 80 % of the plants emerge and have a healthy appearance. In the control pots, only the occasional emerged plant, with a diseased appearance, is observed.

Example B18: Residual-protective action against *Cercospora arachidicola* on groundnut plants

Groundnut plants 10-15 cm in height are sprayed to drip point with an aqueous spray mixture (0.02% active ingredient mixture) and infected 48 hours later with a conidia suspension of the fungus. The plants are incubated for 72 hours at 21°C and high humidity and then placed in a greenhouse until the typical leaf specks appear. Evaluation of the activity of the active ingredient is made 12 days after infection and is based on the number and size of the leaf specks.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A2 to A5 and A7 to A12 bring about a reduction in leaf specks to less than approx. 10 % of the leaf surface. In some cases, the disease is inhibited completely (0-5% infestation).

Example B19: Action against *Puccinia graminis* on wheat

a) Residual protective action:

6 days after sowing, wheat plants are sprayed to drip point with an aqueous spray mixture (0.02 % active ingredient mixture) and infected 24 hours later with a uredospore suspension of the fungus. The plants are then incubated for 48 hours (conditions: 95-100 % relative humidity and 20°C) and then placed in a greenhouse at 22°C. Evaluation of rust pustule development is made 12 days after infection.

b) Systemic action:

Wheat plants are watered 5 days after sowing with an aqueous spray mixture (0.006 % active ingredient mixture, based on the volume of the soil). Care is taken that the spray

mixture does not come into contact with the parts of the plants above the soil. 48 hours later the plants are infected with a uredospore suspension of the fungus. The plants are then incubated for 48 hours (conditions: 95-100 % relative humidity and 20°C) and then placed in a greenhouse at 22°C. Evaluation of rust pustule development is made 12 days after infection.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A1 to A18 bring about a marked reduction in fungus infestation, in some cases to 10-0 %.

Example B20: Action against *Pyricularia oryzae* on rice

a) Residual-protective action:

After a cultivation period of 2 weeks, rice plants are sprayed to drip point with an aqueous spray mixture (0.02 % active ingredient mixture) and infected 48 hours later with a conidia suspension of the fungus. Evaluation of fungus infestation is made 5 days after infection, during which time a relative humidity of 95-100 % and a temperature of 22°C are maintained.

b) Systemic action:

2-week-old rice plants are watered with an aqueous spray mixture (0.006% active ingredient mixture, based on the volume of the soil). Care is taken that the spray mixture does not come into contact with the parts of the plants that are above the soil. The pots are then filled with water so that the lowermost parts of the stems of the rice plants stand in water. After 96 hours, the plants are infected with a conidia suspension of the fungus and then kept for 5 days at 95-100% relative humidity and a temperature of 24°C.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A7 to A9 and A14 to A18 largely prevent the disease from breaking out on the infected plants.

Example B21: Residual protective action against *Venturia inaequalis* on apples

Apple cuttings with 10-20 cm long fresh shoots are sprayed to drip point with a spray mixture (0.02 % active ingredient mixture) and infected 24 hours later with a conidia suspension of the fungus. The plants are then incubated for 5 days at 90-100 % relative humidity and placed in a greenhouse for a further 10 days at 20-24°C. Scab infestation is evaluated 15 days after infection.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A1 to A18 mainly exhibit sustained activity against scab diseases.

Example B22: Action against Erysiphe graminis on barley

a) Residual-protective action:

Barley plants about 8 cm in height are sprayed to drip point with an aqueous spray mixture (0.02 % active ingredient mixture) and dusted 3 to 4 hours later with conidia of the fungus. The infected plants are placed in a greenhouse at 22°C. The fungus infestation is evaluated 10 days after infection.

b) Systemic action:

An aqueous spray mixture (0.002% active ingredient mixture, based on the volume of the soil) is used to water barley plants about 8 cm in height. Care is taken that the spray mixture does not come into contact with the parts of the plants above the soil. The plants are dusted 48 hours later with conidia of the fungus. The infected plants are then placed in a greenhouse at 22°C. The fungus infestation is evaluated 10 days after infection.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A1 to A18 are generally able to reduce disease infestation to less than 20 %, and in some cases even completely.

Example B23: Action against Podosphaera leucotricha on apple shoots

Residual-protective action

Apple cuttings with about 15 cm long fresh shoots are sprayed with a spray mixture (0.06 % active ingredient mixture). After 24 hours, the treated plants are infected with a conidia suspension of the fungus and are placed in a climatic chamber at 70 % relative humidity and 20°C. Fungus infestation is evaluated 12 days after infection.

The compositions according to the invention exhibit good activity in this test. In particular, following treatment with compound mixtures A1 to A18 disease infestation is less than 20 %. Control plants exhibit 100 % infestation.

Example B24: Action against Botrytis cinerea on apple fruits

Residual-protective action

Artificially damaged apples are treated by dropping a spray mixture (0.02 % active ingredient mixture) onto the damaged sites. The treated fruits are then inoculated with a

spore suspension of the fungus and are incubated for one week at high humidity and about 20°C. The fungicidal activity of the test compound is derived from the number of rotting damaged sites.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A1 to A18 are able to prevent the rot from spreading almost completely.

Example B25: Action against *Helminthosporium gramineum*

Wheat grains are contaminated with a spore suspension of the fungus and are left to dry. The contaminated grains are dressed with a suspension of the test compound (600 ppm active ingredient mixture, based on the weight of the seeds). Two days later, the grains are placed on suitable agar dishes and, after a further four days, the development of the fungus colonies around the grains is assessed. The evaluation of the test compound is based on the number and size of the fungus colonies.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A1 to A18 exhibit good activity, i.e. inhibition of the fungus colonies.

Example B26: Action against *Colletotrichum lagenarium* on cucumbers

After a cultivation period of 2 weeks, cucumber plants are sprayed with a spray mixture (concentration of active ingredient mixture: 0.002%). Two days later, the plants are infected with a spore suspension (1.5×10^5 spores/ml) of the fungus and are incubated for 36 hours at 23°C and high humidity. Incubation is then continued at normal humidity and about 22-23°C. The fungus infestation that has occurred is evaluated 8 days after infection. Fungus infestation is 100% on untreated and infected control plants.

The compositions according to the invention exhibit good activity in this test. In particular, compound mixtures A1 to A6 and A17 inhibit infestation with the disease almost completely.

Example B27: Action against *Fusarium nivale* on rye

Rye of the Tetrahell variety which is naturally infected with *Fusarium nivale* is dressed in a roller mixer with the test compound mixture, the following concentrations being used: 20 or 6 ppm active ingredient mixture (based on the weight of the seed).

The infected and treated rye is sown in October in the open with a seeder in plots 3 metres long and in 6 rows. Three replicates are carried out with each concentration.

- 36 -

Until evaluation of the infestation is made, the test crop is cultivated under normal field conditions (preferably in a region with unbroken snow cover during the winter months).

In order to evaluate the phytotoxicity, the emergence is assessed in the autumn and the crop density/number of plants per unit area is assessed in the spring.

To determine the activity of the test compounds, the percentage of plants attacked by *Fusarium* is assessed in the spring directly after the snow has melted. The number of infested plants is less than 5% in the present case. The plants that have emerged have a healthy appearance.

The compositions according to the invention exhibit good activity in this test. In particular, following treatment with compound mixtures A1 and A11 to A18 infestation is completely suppressed.

Example B28: Action against *Septoria nodorum* on wheat

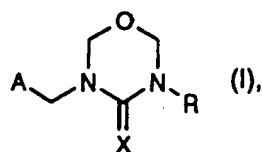
Wheat plants are sprayed at the 3-leaf stage with a spray mixture (60 ppm active ingredient mixture) prepared from a wettable powder formulation of the test compounds (2.8:1).

24 hours later, the treated plants are infected with a conidia suspension of the fungus. The plants are then incubated for 2 days at 90-100% relative humidity and are placed in a greenhouse for a further 10 days at 20-24°C. Fungus infestation is evaluated 13 days after infection. Less than 1% of the wheat plants are infested.

The compositions according to the invention exhibit good activity in this test. In particular, following treatment with compound mixtures A1, A5 to A8 and A14 infestation is completely suppressed.

What is claimed is:

1. A composition for controlling insects or representatives of the order Acarina and microorganisms, which composition comprises at least one compound of formula

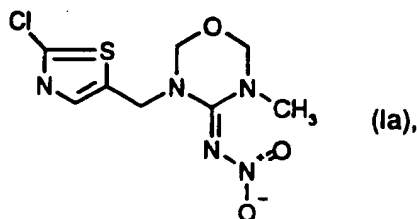


wherein

- A is an unsubstituted or mono- to tetra-substituted aromatic or non-aromatic, monocyclic or bicyclic, heterocyclic radical, one or two of the substituents of A being selected from the group consisting of: halo-C₁-C₃alkyl, cyclopropyl, halocyclopropyl, C₂-C₃alkenyl, C₂-C₃alkynyl, halo-C₂-C₃alkenyl, halo-C₂-C₃alkynyl, halo-C₁-C₃alkoxy, C₁-C₃alkylthio, halo-C₁-C₃alkylthio, allyloxy, propargyloxy, allylthio, propargylthio, haloallyloxy, halo-allylthio, cyano and nitro, and from one to four of the substituents of A being selected from the group consisting of: C₁-C₃alkyl, C₁-C₃alkoxy and halogen;
- R is hydrogen, C₁-C₆alkyl, phenyl-C₁-C₄alkyl, C₃-C₆cycloalkyl, C₂-C₆alkenyl or C₂-C₆alkynyl; and
- X is N-NO₂ or N-CN,

or, where appropriate, a tautomer thereof, in each case in free form or in salt form, at least one microbicidal compound, and at least one adjuvant, and, where appropriate; at least one further insecticidal compound.

2. A composition according to claim 1 which comprises a compound of formula



and one or more compounds selected from the substance classes consisting of azoles, cyanopyrroles and acylalanines.

3. A composition according to claim 1 which comprises in addition to a the insecticidally active compound of formula (I) one or two microbicidal compounds.
4. A composition according to any one of claims 1 to 3 which comprises in addition to a compound of formula (I) also one or two of the following compounds: cyproconazole, cyprodinil, difenoconazole, epoxiconazole, fenpiclonil, fludioxonil, flutriafol, furalaxyl, hymexazol, imazalil, metalaxyl, R-metalaxyl, penconazole, propiconazole, tebuconazole, tefluthrin, triazoxide or triticonazole.
5. A composition according to any one of claims 1, 3 and 4 which comprises a compound of formula (I) wherein A is an unsubstituted or mono- to tetra-substituted, aromatic or non-aromatic, monocyclic or bicyclic, heterocyclic radical, one or two of the substituents of A being selected from the group consisting of: halo-C₁-C₃alkyl, cyclopropyl, halocyclopropyl, C₂-C₃alkenyl, C₂-C₃alkynyl, halo-C₂-C₃alkenyl, halo-C₂-C₃alkynyl, halo-C₁-C₃alkoxy, C₁-C₃alkylthio, halo-C₁-C₃alkylthio, allyloxy, propargyloxy, allylthio, propargylthio, haloallyloxy, haloallylthio, cyano and nitro, and from one to four of the substituents of A being selected from the group consisting of: C₁-C₃alkyl, C₁-C₃alkoxy and halogen;
R is hydrogen, C₁-C₆alkyl, C₃-C₆cycloalkyl, C₂-C₆alkenyl or C₂-C₆alkynyl; and
X is N-NO₂ or N-CN.
6. A composition according to any one of claims 1 and 3 to 5 which comprises a compound of formula (I) wherein the basic ring structure of A contains from 1 up to and including 4 hetero atoms.
7. A composition according to any one of claims 1 and 3 to 6 which comprises a compound of formula (I) wherein the basic ring structure of A contains 1, 2 or 3 hetero atoms selected from the group consisting of oxygen, sulfur and nitrogen, not more than one of the hetero atoms present in the basic ring structure being an oxygen atom and not more than one of the hetero atoms present in the basic ring structure being a sulfur atom.
8. A composition according to any one of claims 1 and 3 to 7 which comprises a compound of formula (I) wherein A is unsubstituted or mono- or di-substituted by substituents selected from the group consisting of halogen, C₁-C₃alkyl, halo-C₁-C₃alkyl, C₁-C₃alkoxy and halo-C₁-C₃alkoxy.

9. A composition according to any one of claims 1 and 3 to 8 which comprises a compound of formula (I) wherein the basic ring structure of A is a pyridyl, 1-oxidopyridinio or thiazolyl group.
10. A composition according to any one of claims 1 and 3 to 9 which comprises a compound of formula (I) wherein R is C₁-C₆alkyl, phenyl-C₁-C₄alkyl, C₃-C₆cycloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl.
11. A composition according to any one of claims 1 and 3 to 10 which comprises a compound of formula (I) wherein X is N-NO₂.
12. A composition according to any one of claims 1 and 3 to 11 which comprises a compound of formula (I) wherein A is a 2-chloropyrid-5-yl, 2-methylpyrid-5-yl, 1-oxido-3-pyridinio, 2-chloro-1-oxido-5-pyridinio, 2,3-dichloro-1-oxido-5-pyridinio or 2-chlorothiazol-5-yl group and R is C₁-C₄alkyl.
13. A composition according to any one of claims 1 and 3 to 12 which comprises a compound of formula (I) wherein A is a 2-chlorothiazol-5-yl or 2-chloropyrid-5-yl group, R is C₁-C₄alkyl and X is N-NO₂.
14. A composition according to any one of claims 1 to 13 which comprises a compound of formula (I) and fludioxonil.
15. A composition according to any one of claims 1 to 14 for controlling insects or representatives of the order Acarina and phytopathogenic fungi.
16. A composition according to any one of claims 1 to 15 for controlling feeding insects and phytopathogenic fungi.
17. A process for the preparation of a composition according to claim 1, which comprises homogeneously mixing and/or grinding the active ingredients with the adjuvant(s).
18. A method of controlling pests and microorganisms, which comprises applying a composition according to claim 1 to the pests and microorganisms or to the habitat thereof.
19. A method according to claim 18 of controlling insects, representatives of the order Acarina and phytopathogenic fungi.
20. A method according to claim 18 of controlling feeding insects.
21. A method according to claim 18 of protecting plant propagation material, which comprises treating the propagation material or the site of planting the propagation material.

22. Plant propagation material treated in accordance with the method described in claim 21.
23. The use of a composition as described in any one of claims 1 to 16 in a method as described in any one of claims 18 to 21.

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No
PCT/EP 96/05489

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N43/88 A01N51/00 //(A01N43/88,53:00,43:707,43:653,43:54,
43:36,37:22),(A01N51/00,53:00,43:707,43:653,43:54,43:36,37:22)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 580 553 A (CIBA GEIGY AG) 26 January 1994 cited in the application See: compound 2.3; p. 15, lines 17-25; Examples B1,B2,B5,B12,B13. ---	1-23
Y	PATENT ABSTRACTS OF JAPAN vol. 095, no. 011, 26 December 1995 & JP 07 224062 A (NIPPON BAYERAGROCHEM KK), 22 August 1995, see abstract ---	1-23
Y	WO 95 00303 A (BAYER AG ;HEUER LUTZ (DE); KUGLER MARTIN (DE); BUSCHHAUS HANS ULRICH) January 1995 see page 5, line 25; claim 7 --- -/--	1-23



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * "A" document member of the same patent family

Date of the actual completion of the international search

14 April 1997

Date of mailing of the international search report

29 -04- 1997

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Klaver, J

INTERNATIONAL SEARCH REPORT

Intern. Patent Application No

PCT/EP 96/05489

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 545 834 A (RHONE POULENC AGROCHIMIE) 9 June 1993 see the whole document ---	1-23
A	US 5 430 035 A (ZEUN RONALD ET AL) 4 July 1995 see the whole document ---	1-23
A	WO 94 08976 A (DU PONT ; LETT RENEE MARIE (US)) 28 April 1994 see page 25, line 29 - page 26, line 24 -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/05489

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0580553 A	26-01-94	AU 4210793 A	27-01-94
		BG 97962 A	25-04-94
		BR 9302943 A	16-02-94
		CA 2100924 A	23-01-94
		CN 1084171 A	23-03-94
		CZ 9301457 A	16-02-94
		HR 931073 A	30-04-96
		HU 65131 A	28-04-94
		JP 6183918 A	05-07-94
		NZ 248195 A	27-02-96
		PL 299755 A	05-04-94
		SK 76493 A	08-06-94
		ZA 9305263 A	09-02-94
WO 9500303 A	05-01-95	DE 4320495 A	22-12-94
		DE 4406819 A	07-09-95
		AU 7123194 A	17-01-95
		BR 9407120 A	03-09-96
		CA 2165560 A	05-01-95
		EP 0705160 A	10-04-96
		FI 956113 A	19-12-95
		JP 8509437 T	08-10-96
		NO 955107 A	15-12-95
EP 0545834 A	09-06-93	FR 2684519 A	11-06-93
		AP 351 A	09-08-94
		AU 2978992 A	10-06-93
		BR 9204924 A	08-06-93
		CA 2084140 A	07-06-93
		CN 1072817 A	09-06-93
		FI 925532 A	07-06-93
		HR 921391 A	31-12-95
		JP 5246806 A	24-09-93
		SK 358292 A	08-03-95
		ZA 9209342 A	04-06-93
US 5430035 A	04-07-95	US 5519026 A	21-05-96
		US 5536726 A	16-07-96
		AU 6599094 A	05-01-95
		BG 98869 A	31-03-95

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/05489

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5430035 A		BR 9402556 A	28-03-95
		CA 2126714 A	29-12-94
		CN 1099220 A	01-03-95
		CZ 9401564 A	18-01-95
		EP 0630569 A	28-12-94
		HU 67004 A	30-01-95
		JP 7017811 A	20-01-95
		NZ 260840 A	27-11-95
		PL 303960 A	09-01-95
		SI 9400265 A	31-12-94
		SK 76794 A	05-01-95

WO 9408976 A	28-04-94	AU 5165093 A	09-05-94

Form PCT/ISA/210 (patent family annex) (July 1992)